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ON SEWAGE TREATMENT AND WATER POLLUTION.
A REVIEW OF THE LITERATURE

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Robert A. Taft Sanitary Engineering Center
Cincinnati, Ohio

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A REVIEW OF THE LITERATURE

U. S. DEPARTMENT OF
HEALTH, EDUCATION, AND WELFARE
Public Health Service
Robert A. Taft Sanitary Engineering Center
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Synthetic Detergents and Their Effects
on Sewage Treatment and Water Pollution

A Review of the Literature

Russell S. Smith*, Graham Walton**, and Jesse M. Cohen***

The rapidly increased use of synthetic detergents, particularly for household purposes, during recent years has given rise to a series of problems affecting operators of sewage and water treatment plants, stream pollution control authorities and others.

Many articles concerning synthetic detergents and their effect on water pollution have appeared in the technical literature in the last seven years. Much of the information given is confusing and apparently contradictory, due in no small part to confusion in terms in describing the various materials.

For this reason, it would seem proper to include definitions of some of the terms used in this review. These definitions are both tentative and restrictive, rather than all inclusive. For example, the definition of detergent as used herein has been restricted to soaps and synthetic detergents, rather than the broad definition which would include any cleaning agent, such as water or other solvents.

DEFINITION OF TERMS.

Surfactant (Surface Active Agent) - any organic compound which affects interfacial tension. Although soap is such a material, the term as used applies to the organic derivatives (e.g. sodium alkyl aryl sulfonates, alkyl sulfates, alkyl sulfonates, etc., of relatively high molecu-

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lar weight) which are used as detergents, wetting agents, penetrants, spreaders, dispersants, foamants or related purposes.

Manufactured Surfactant - a surfactant material in either liquid, slurry or dried form. It generally contains contaminants resulting from the manufacturing process. These contaminants have been left in the material to reduce hygroscopicity and improve handling quality or because their removal is not economically justified.

Detergent - a substance or mixture that has cleaning action due to a combination of properties including the lowering of the surface tension, and wetting, emulsification and dispersive actions (e.g. soap and synthetic detergents).

Soap - a metallic salt or mixture of salts of the various fatty acids of natural oils or fats. Essentially the product of boiling an oil or a fat with a strong caustic.

Synthetic Detergent - a non-soap product having detergent properties. Its metal salts are not precipitated from hard water and it is reasonably stable to acid and alkali. It is compounded from a manufactured surfactant with additive materials to enhance its detergent and other characteristics.

Industrial Synthetic Detergent - a synthetic detergent compounded from a manufactured surfactant with or without additive material to serve a particular industrial cleaning purpose.

Household Synthetic Detergent - a synthetic detergent compounded from a manufactured surfactant with additive materials, such as phosphates, silicates, fluorescent dyes and perfumes, and which is prepared primarily for household use. Although normally packaged for retail store trade, it may be sold in large containers for use in laundries, restaurants and institutions.

Builders.— Inorganic or organic salts added to manufactured surfactants to enhance their detergent properties. Among these substances are various polyphosphates, silicates, sodium carboxymethylcellulose, etc.

EXTENT OF DETERGENT USE

The rapid increase in the use of synthetic detergents during the post World War II period is shown in Table I, which summarizes data presented by Terry (83) and others (62) (78) (5) (6).

Table I. COMPARISON OF PRODUCTION AT FACTORY LEVEL OF SOAP AND MANUFACTURED SURFACTANTS.

Year	Production in Million Pounds Soap	Manufactured Surfactants	Per Cent of Total Market Secured by Manufactured Surfactants
1940	2,648	65.5	2.4
1945	2,872	184.4	6.0
1950	2,500	1,200	32.4
1951		1,400	36
1952	2,200	1,750	44
1953 (6 mo)	803	902	52.7
(9 mo)		1,425	

According to Terry (83), 80% or 1,400 million pounds of the manufactured surfactants produced in 1952 were processed to make 2,200 million pounds of household synthetic detergents. This amounted to 53% of the household detergents, and members of the industry anticipate it will grow to 70 or 75 per cent of the total household detergent market.

Terry (83) notes, "Over 800 surfactants are commercially available by brand name in the U. S. today, but only a few have any significance on a volume basis". The 1952 production, based on 100% active surfactant basis, was as follows:

400	million pounds of alkyl aryl sulfonates
113	" " " alkyl sulfates
95	" " " nonionics

Present capacity of plants in the U. S. is estimated at between 800 and 900 million pounds annually, and is divided as follows: 43% alkyl aryl sulfonates, 12% alkyl sulfates, 12% nonionics, and 33% miscellaneous.

It is anticipated that the alkyl aryl sulfonates, because of their low cost and versatility, will continue in high production; and that the production of nonionics will increase at a slightly greater rate than in the past.

CHEMISTRY OF SYNTHETIC DETERGENTS

There are many articles in the literature on the chemistry of surfactants and the principles of their behavior, and a number of books have been published on the subject. Of the many sources consulted, certain texts (60)(67)(70)(73)(82) have proved very useful.

The date when the first synthetic detergents were produced depends principally on the terminology used. Although sulfonated vegetable oils have been known since 1831, and have been in use, principally in the textile trades, since 1875, many believe that the first true synthetic detergent was described in a German patent in 1916 on the production of diisopropyl naphthalene sodium sulfonate. Much of the impetus for the new detergent industry arose in Germany during World War I, when the shortage of natural fats led to the search for "ersatz" materials. This development provided an opportunity for overcoming some of the serious disadvantages in the use of ordinary soap, resulting from its instability to hard water and to acid.

Classification. A review of the fundamental principles of detergency and of the physico-chemical properties of detergent solutions will enable an explanation of their characteristic behavior. Surface active agents are recognized as substances which in dilute solution

are responsible for wetting, emulsification, dispersing, foaming and related phenomena. These compounds, as prepared in industry, ordinarily consist of complex mixtures of isomers or homologues which result from the nature of the raw material used.

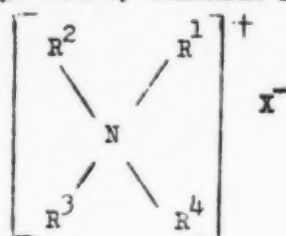
For any given compound to display surface activity, there must be present in the molecule a hydrophobic hydrocarbon-portion, to which is attached one or more hydrophilic groups. Since most of these compounds dissociate in solution, it is possible to classify them into anionic, cationic and nonionic surfactants according to their ionization.

The molecules of anionic surfactants dissociate in solution to yield a predominantly hydrocarbon anion of large mass and a cation of small mass. The majority of commercial surfactants belong to this class, which includes:

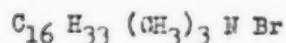
Sulfated fatty alcohols	e.g. sodium dodecyl sulfato
$(R - O SO_3)^- Na^+$	$C_{12} H_{25} O SO_3 Na$
Sulfonated hydrocarbons	e.g. dodecyl benzene sodium sulfonate
$(R - SO_3)^- Na^+$	$C_{12} H_{25} - C_6 H_5 - SO_3 Na$
Sulfonated fatty acid condensates	e.g. oleyl methyl taurine
$(R - CO - R^1 SO_3)^- Na^+$	$C_{17} H_{33} CON(CH_3)CH_2CH_2SO_3Na$
Sulfonated dibasic esters	e.g. sodium dioctyl monosulfosuccinate
$Na^+ \left[\begin{array}{c} CH_2 COOR \\ \\ SO_3 - CH COOR \end{array} \right]$	$\begin{array}{c} CH_2 - COO C_8 H_{17} \\ \\ CH - COO C_8 H_{17} \\ \\ Na SO_3 \end{array}$

Cationic surfactants dissociate in solution to give a cation of large mass and an anion of small mass. Although numerous cationic surfactants may be synthesized, two main types predominate. These are:

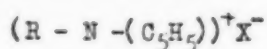
Quaternary ammonium salts



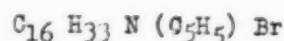
e.g. cetyl trimethyl ammonium bromide



Pyridinium salts

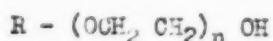


e.g. cetyl pyridinium bromide



Unlike the other two classes, nonionic surfactants are not dissociated in solution. This class is exemplified by:

1. Ethylene oxide - alcohol or phenol condensates



Physical Properties. Surfactants exhibit two main effects due to their hydrophilic-hydrophobic nature. One is their ability to concentrate at interfaces and the second is their ability to form micelles. These tendencies to orientate and to aggregate are reflected in many of the characteristic physical and chemical properties of surfactant solutions, such as osmosis, electrical conductivity, boundary tensions, solubility, and foaming and emulsifying powers. A short description of these properties follows:

The need for detergents arises from the well-known fact that oil and water do not mix. Washing processes involve the removal of "dirt", which is almost always greasy in character, from a substrate such as human skin, textiles or metals. Water itself is quite useless for this purpose since it will not spread uniformly over a greasy surface. The first requirement of a detergent is that it shall be able to spread over such a surface.

Surfactants in solution are able to cause "wetting" since they are capable of being oriented at an oil-water interface, thereby acting as an

anchor between the two phases. At the same time their ability to become concentrated at an air-liquid surface causes a reduction in surface tension of the liquid. Wetting of the soiled substrate by a detergent solution is only the first requirement. Other factors, including the detachment of dirt from the substrate and its subsequent removal as an emulsion, suspension, or in the foam, are equally important.

Surface tension is a fundamental property of liquids. A molecule at the surface of an unrestrained liquid, such as a droplet of water, is subjected to a highly unbalanced force field. On the liquid side of the molecule the attractive force of the other similar molecules is as strong as in the interior. On the vapor side there is only the attractive force of widely scattered gas molecules. Since the attraction for a surface molecule exerted by the vapor above it is inconsequential, there exists a resultant on every surface molecule tending to pull it perpendicularly inward. This force acts in such a way that the surface strives to assume a shape having the smallest possible area for the enclosed volume. The force tending to restrict the surface area is termed surface tension. The term interfacial tension includes surface tension but by common usage generally refers to the force between immiscible liquids or between a solid and liquid, whereas surface tension refers to the forces between a gas and liquid. The aqueous solutions of most inorganic salts show a higher surface tension than that of pure water. Most water soluble organic compounds lower the surface tension, and surfactants show this to an extreme degree.

In any solution one is dealing with several interdependent properties, those of the surface and those in the main body of the liquid. The unusual surface behavior of surfactants corresponds to unusual

properties of the interior of the solution. One property common to all surfactants is their ability to aggregate in solution and become colloidal. This aggregation is reflected by marked changes in osmotic activity, electrical conductivity, interfacial activity, etc. At a certain concentration, characteristic for each individual surfactant, a number of molecules or ions combine to form a colloidal unit called a "micelle". It is generally accepted that these micelles form in large amounts only when a definite concentration range is reached and that their formation is reflected in many simultaneous changes in physical and chemical properties of the solution.

Foam or froth may be defined as a measurably stable honeycomb structure of gas cells (air usually) whose walls consist of thin liquid films. It is generally conceded that pure liquids do not foam, and that many different types of solutions besides those containing surfactants have foaming power. While the mechanism of how foams are formed is not clear, the manner by which foams disappear or are destroyed is relatively simple. The liquid drains out from between the two parallel surfaces of the individual films, thereby causing the film to become progressively thinner. At a certain critical thickness, the film collapses. Evaporation will hasten the thinning of foam films. Foams may also be broken mechanically by deformation of the individual bubbles or by the addition of "anti-foam" agents. Solids and protective colloids prevent coalescence of foam bubbles. The stabilizing action of a solid in a foam system depends upon the degree of dispersion of the solid and its nature, affinity, and concentration.

Emulsions are systems consisting of one liquid, the dispersed phase, suspended as minute droplets in another liquid, the continuous phase. The main criterion for the formation of emulsions, at least for

stable liquid-in-liquid dispersions, is that a suitable third phase be present. This third phase, the emulsifying agent, may be any of several substances, liquid or solid. The lowering of interfacial tension is one of the factors contributing to ease of emulsification.

Builders. Builders used as adjuncts to synthetic detergents may be divided into chemical classes, as follows:

- (a) Alkali salts, usually the sodium salt of weak inorganic acids, such as sodium carbonate, sodium silicates, the sodium phosphates and sodium borates.
- (b) Sodium or potassium hydroxide.
- (c) Neutral inorganic salts, usually the sodium salt of strong inorganic acids.

In addition, there are other materials, which are added to household synthetic detergent formulations such as sodium carboxymethylcellulose, optical dyes, perfumes, etc.

The surface activity of surfactants is said to be affected appreciably by salts or other electrolytes in solution. Surface and interfacial tensions are lowered because of the effects of the ions derived from the salts on micelle formation. Probably the most significant role of builders in synthetic detergent formulation is that of increasing deterative action by enhancing surface active properties and by acting as suspending and dispersing agents. Other effects of builders are neutralization, softening by sequestering action, and pH control.

ANALYTICAL PROCEDURES.

Analytical procedures for synthetic detergents in water pollution chemistry are aimed at qualitative and quantitative determination of the various surfactants. Due to the complex and diverse nature of these organic compounds, methods for their determination have been separated

into three classes - anionics, nonionics and cationics. A brief discussion of analytical procedures for anionic and nonionic materials, as determined by a limited search of the literature, follows. Analytical methods for the cationics have not been included as these compounds are not used extensively and, in general, will react with anionics present in wastes to form insoluble precipitates.

Anionic Surfactants. Methods which have been used to measure the concentration of anionic surfactants can be listed as follows:

1. Gravimetric, following isolation of organic compound.
2. Titration with sodium hydroxide after hydrolysis.
3. Determination of sulfate ion after hydrolysis.
4. Colorimetric determination using various dyestuffs.
5. Formation of an amine-surfactant salt followed by titration with sodium hydroxide.
6. Turbidimetric.
7. A "two-phase" titration method.
8. Polarographic.
9. Infra-red adsorption technique.

A method was proposed by Hart (42) in which the organically combined sulfuric anhydride of some surfactants could be determined by isolating the sulfated or sulfonated compound free from inorganic salts by extracting with ether in the presence of a strong solution of sodium chloride and then determining the ash of the purified product. In order to extend the application of this method to more highly sulfated or sulfonated compounds Hart (43) suggested a method based on the observation that the sodium or potassium salt of the sulfated or sulfonated product, when shaken with a concentrated solution of ammonium chloride, is quantita-

tively converted into its ammonium salt, and reverts to the sodium salt when shaken with sodium sulfate solution. This method was further extended by Hart (44) to include the determination of organic matter in surfactants.

Biffen and Snell (12) reviewed the early methods of analysis of alcohol and alkyl sulfates. The increase in acidity following acid hydrolysis and extraction with alcohol was titrated with 0.5 N sodium hydroxide. Also, the sulfate ion could be determined by the well-known benzidine method. All of the above analyses were applied to dry powder mixtures. The fact that certain cationic surface-active agents, such as cetyl pyridinium bromide, form stoichiometric, water insoluble salts with anionic surface-active agents such as the alkyl sulfates, alkyl sulfonates, and alkyl aryl sulfonates, has been used as the basis of a titrimetric method of analysis of the latter materials. The method of Hartley and Runnicles (41) uses brom phenol blue as an indicator to detect when excess cation-active material has been added.

Harris (40) reported that few of the published methods of Hart (42) (44) were entirely satisfactory, as impurities such as sodium sulfate interfered. He devised a method sensitive to 1 ppm of pure sulfonate by using the reaction of o-tolidine and sodium hypochlorite which produces a blue color with some surface active agents and which could then be read visually or in a photometer.

Jones (51) described a colorimetric procedure which depends upon two observations: (a) that methylene blue hydrochloride is insoluble in chloroform, and (b) that anionic surfactants will form a colored methylene blue-anionic surfactant complex which can be quantitatively extracted from aqueous solution with chloroform. The intensity of the

color was measured in a photometer. The reaction is stoichiometric.

Marren and Schifferli (66) proposed a method based on the fact that, under standardized conditions, p-toluidine hydrochloride reacts with organic sulfonates to give amino-sulfonate salts which can be titrated, after extraction from the aqueous solution with carbon tetrachloride, with standard alkali with a suitable indicator.

Lambert (55) determined the concentration of surface active colloidal electrolytes with cationic agents (or vice versa) under such conditions that a colloidal precipitate was produced near the equivalence point. The end point of the titration was shown by the maximum turbidity of the solution.

Barr et al (9) proposed a titration method, based on a combination of the Hertley and Runnicles (41) and Jones (51) procedures, which is essentially the same as that published by Epton (25). The determination used a partition end point dependent on the solubility in organic solvents of complexes formed between anion active agents and basic dyes such as methylene blue, and between cation active agents and acid dyes, such as brom. phenol blue. Thus, anionic surfactants can be titrated with a standard solution of a pure cationic agent such as cetyltrimethylammonium bromide. The titration is performed by layering an aqueous solution of anionic surfactant plus methylene blue indicator over chloroform. The end point is indicated when the blue color is just discharged from the chloroform layer.

The work of Jones (51) was extended to include dyes other than methylene blue. Thus, Karush and Sonenberg (52) used rosaniline hydrochloride and extracted the colored complex with a mixed organic solvent, 50% chloroform and 50% ethyl acetate. Solutions of alkyl sulfates as

dilute as 5×10^{-6} molar could be analyzed with an accuracy of about 2%. The molecular ratio of dye to surfactant was found to be stoichiometric, an experimental value of 0.94 to 1.0 was obtained. Basic fuchsin was used by Wallin (89). The dye reacts with anionic surfactants to form a chloroform soluble fluorescent complex, the intensity of which can be measured photometrically.

The methylene blue extraction method with some modifications was also used by Faust (27) and by Lester and Raybould (57). The latter found that high results were obtained when nitrates, thiocyanates, or certain organic compounds were present. In order to eliminate these interferences, Evans (26), Kay (53) and Hurley (49) extracted the colored methylene blue - anionic active complex at two pH's, 3.25 and 0.7, and then extrapolated a line drawn through these points to pH minus 2. Dogons et al (20) extended the method of Jones (51) to enable the differentiation between total-, sulfonate-, and sulfate-anionic active content. A detailed study of the factors affecting this method was also made by Dogons et al (21).

Edwards et al (24) applied a chromatographic technique by absorbing a methylene blue - cetyl sulfate complex on ground quartz, extruding the column, eluting with alcohol and determining the intensity of color photometrically. In the range 10 - 40 mg per liter, the deviation from the mean of duplicate analyses was 0.17 ± 0.15 mg per liter.

Lewis and Horndon (58) examined the turbidimetric method of analysis proposed by Lambert (55) and the "two-phase" titration method originally devised by Epton (25) and concluded that the "two-phase" titration method was preferable and gave an indication of satisfactory performance in the presence of a number of organic substances.

Von Stackelberg and Schutz (81) used a polarographic method for the determination of surfactants based on the fact that surface active agents decrease the maximum height of polarograms by adsorption at the mercury-solution interface. The decrease in height depends on the content of surfactant in solution.

Infra-red spectrograms were used by Sadtler (72) to identify the functional groups of surfactants.

Non-ionic Compounds. At the present time this class of surfactants is not used widely in large amounts, although production and use of these substances are increasing. The analytical work on these compounds has been exceedingly sparse, and the problem is further confounded by the bewildering array of types of compounds that make up this class of surface active substances.

Shaffer and Critchfield (77) used silico tungstic acid and barium chloride in an acid solution to precipitate polyglycols. The precipitate was washed, dried and ignited at 700° C to the mixed oxides of barium, silicon and tungsten. The amount of polyglycol present was calculated by an empirical factor determined from known quantities. In a colorimetric modification these authors used phosphomolybdic acid and barium chloride to precipitate the polyglycol. Molybdenum in the residue was determined colorimetrically. The gravimetric procedure was suitable for quantities of 5-100 mg of polyglycol and the useful range of the colorimetric modification was 0.05 - 1.0 mg with a minimum concentration of 0.01 mg per ml.

Oliver and Preston (69) applied the phosphomolybdic precipitation method to ethylene oxide type of nonionics. The method was applicable only to solutions containing a known nonionic surfactant, both as to type

and molecular weight. Phosphomolybdic acid was also used by Heatley and Page (45) to precipitate polyglycols. The precipitate was dissolved in methylcellosolve and the absorption determined in a Bockman Model DU spectrophotometer at 310 mμ. Amounts up to 150 micrograms in 4 ml could be determined with an error of about ± 1 microgram. The surfactant could be concentrated from sewage by extraction with ether and a strong solution of sodium chloride.

SEWAGE TREATMENT.

Frothing. The effect of the increasing use of synthetic detergents on sewage treatment processes which is most apparent and thus most often reported by plant operators has been excessive frothing on aeration tanks. The first occurrence of extreme frothing reported in the literature was at Mt. Penn, Pa. (2). It was later found that samples of a household synthetic detergent (stated to be nonionic) had been distributed to housewives throughout the community on Friday. By Monday morning, froth 2 to 5 feet deep enveloped most of the mechanical aeration activated sludge plant. After two weeks the froth decreased in amount, but was still evident each morning for thirty days (78). Frothing has been reported from many other activated sludge plants in this country and abroad. Among the plants that reported frothing difficulties were Bartlesville, Okla. (3), where the superintendent is reported to believe that synthetic detergents inhibit to some extent the growth of aerobic bacteria; Batavia, Ill. (4), where it was stated that the settling quality of the mixed liquor solids became very poor; Rockville, Md., and Triangle, Va. (78); Baltimore, Md. (54); New York City, Los Angeles, Philadelphia and Nassau County, Long Island (39). Froth to a depth of 14 ft. above the water surface has been reported on a diffused air activated sludge plant at Motherwell, England, by McNicholas (63). McNicholas stated that large amounts of foam first occurred in

September, 1952, and it was later found that this corresponded with the introduction of the household detergent Tide into the district.

This froth may be an accident hazard as it smoars the tank walls and walkways with grease and sludge solids, and where it overflows the tank walls it leaves a fatty, sticky substance that chokes grass (4). Donaldson (22) stated that in New York City froth from final tanks or on effluents from the activated sludge plants contained 30 to 50% grease and that some dried froth from tank walls contained up to 90% grease. Heavy frothing is a serious hindrance to plant operation as it makes it impossible to reach and operate air and liquid valves located in the tank area. Wind blown froth may be a significant health hazard. Berg (11) stated that it has been found that the bacterial counts in the foam phase are at least 20 times as great as in the liquid phase at the same relative point in the aeration tank.

Froth on aeration tanks has been controlled at various plants by means of water sprays or by use of defoaming agents. McNicholas (63) at Motherwell, England, describes a method of control by a rainlike spray of final effluent. Simpson (73) mentions the use of spray control at Mt. Penn, Pa. Grooley (39) stated that limited experience indicated that the efficient quantity for defrothing sprays was from 15 to 20 gpm per mgd of sewage, operated continuously except during weak sewage hours, or 0.25 to over 0.50 gpm per foot of aeration tank. Grooley also stated that anti-foam agents have been used at rates of 2.5 to 7.5 lb. per mgd of sewage. The anti-foam agent may be introduced into effluent sprays or into return sludge. Berg (11) stated that frothing can be controlled by proper application of good commercial antifoam at a cost of approximately fifty cents to one dollar per million gallons of sewage. Donaldson (22)

reported that at a New York City plant satisfactory control of severe frothing had been provided by a permanent system of spray piping and injection of anti-foam into the spray system as needed. Neither anti-foam chemical or spray alone was satisfactory. Edwards (93) stated that the silicon anti-foam agents were not satisfactory for New York needs. Apparently none of the defoamers tried had any harmful effect on the activated sludge process. They seemed to lose their effectiveness as they passed through the aeration tanks. There was no effect on purification nor on settling of the mixed liquor solids. Mineral oil has been used as an anti-foam by McNicholas in Motherwell, England (8), and by Brunner in Fort Wayne, Indiana (13). There is some indication that a high concentration of mixed liquor solids in the aeration tanks may aid in controlling frothing. At Cranston, Rhode Island, (8) frothing occurred consistently with mixed liquor solids at 1250 ppm, but has not occurred with solids held at 3000 - 3500 ppm. Kraus (13) stated that mixed liquor solids concentration of 3000 - 5000 ppm seemed best for prevention of frothing. McNicholas (63) increased mixed liquor solids concentration from 700 to 2450 ppm without overcoming frothing trouble.

The evidence connecting frothing to synthetic detergents is inconclusive. Frothing has become a serious problem in many plants since household synthetic detergents came into common use. The Mt. Penn incident (2)(78) is closely related to a sudden surge in detergent usage. In reports of laboratory experiments dealing with the effect of synthetic detergents on activated sludge, frothing is frequently mentioned. Gaillard (33) notes that with 100 ppm of the detergents tried, there was much frothing and a portion of the sludge was carried out of the liquid with the froth. Manzanelli (65) noted that in his activated sludge

experiments aeration was done by continuous mechanical shaking to overcome frothing. Rudolfs, Manganello and Gillman (71) said that with mixed liquor solids of 1000 ppm frothing occurred with addition of Naccanol. Eckenfelder and Hood (23) reported that frothing was encountered at a certain zone of oxidative purification of sewage by plain aeration or activated sludge, that the zone was characterized by high pH and represented the latter part of the carbonaceous oxidation. They remarked, however, that this did not mean that the sewage would not froth if it had a high concentration of detergent. Wells and Schorer (91) in plant scale experiments at San Antonio, Texas, found that frothing could be produced at will by lowering the concentration of mixed liquor solids and that the froth disappeared as the solids concentration was increased again. For conditions obtaining at the time, no frothing occurred with solids maintained above a level of 1400 ppm. The household detergent Tide was added to one aeration tank pass in concentrations of 12-125 ppm of the mixed liquor flow with a mixed liquor solids concentration of about 3300 ppm and no frothing occurred. In one test 90 ppm of Tide was added to a tank with mixed liquor solids concentration of 950 ppm without causing frothing. Gowdy (38) experimented with the addition of a household synthetic detergent to a mechanical aeration activated sludge plant at Bryan, Ohio. The mixed liquor solids concentration was 800 ppm. The detergent was added to the aeration tank influent at a rate of 100 ppm based on sewage flow. No frothing was induced in the aeration tanks and only minor frothing was found in the effluent channel. When the mixed liquor solids were reduced from 800 to 200 ppm without addition of synthetic detergent, froth appeared in the effluent channel, but disappeared again when the solid concentration was increased to the normal 800 ppm. Walker (13) noted that a frothing

phase was almost universal in starting operation of mechanical aeration plants as mixed liquor solids were accumulating, but disappeared with further increase in solids content. One of the writers had similar experiences over 30 years ago while working with a pilot plant treating tannery wastes with diffused air activated sludge. Every time the plant was drained and restarted it went through a period of extreme frothing while the mixed liquor solids were building up.

Sawyer et al (75) (76) in research work at Massachusetts Institute of Technology on biochemical characteristics of synthetic detergents showed clearly the difference in frothing characteristics of several household synthetic detergents at concentrations of 50 ppm in tap water. One, a nonionic, showed no evidence of foam formation. Several others were anionic types with the principal surfactant material an alkyl aryl sulfonate. One of these produced a small amount of weak foam, while others produced copious quantities of rich, firm foam. The different household detergents had varying effects on the rate of solution of dissolved oxygen during diffused air aeration. In general, those that frothed poorly, or not at all, were the ones showing the greatest reduction of the rate of oxygen transfer.

Sedimentation. Synthetic detergents have interfered with chemical coagulation and sedimentation of sewage. This has been noted particularly on a plant scale in the wool textile section of England where sulphuric acid is used as a coagulant and to "crack" the grease emulsions from the wool scouring. The detergents interfered with grease recovery and increased the B.O.D. loading to trickling filters 30-50% (30). Goldthorpe and Nixon (36) in reporting on the effect of Teepol (a 22% active secondary sodium alkyl sulfato) stated that acid precipitation was almost completely

inhibited by 200 ppm of Teopol and that 25 ppm caused considerable interference. Without the use of the sulphuric acid coagulant, 25 ppm of Teopol prevented precipitation of solids in a pH range of 2.55 to 11.50. Hurley (48) in plant scale experiments at Wolverhampton, England, added 50 and 75 ppm of Teopol to a raw sewage with a "Teopol Content" of 18 ppm. The experiment was continued for 6 months. There was no apparent effect on the treatment processes (sedimentation, trickling filters and final settling) and the effluents from the control and experimental sections were very comparable. Manganeli (65) stated that the detergents Macconol NR (alkyl aryl sulfonate, anionic), and Tween 80, (polyoxyethylene sorbitan monooleate, nonionic) showed a decrease in removal of suspended solids and an increase in the grease remaining in the effluent. It might be noted that Tween 80 is listed by McCutcheon (61) as a general emulsifier used to solubilize essential oils and vitamins. The Macconol interfered with flocculation and coagulation when an iron salt at a dosage of 10 ppm of iron was used as coagulant, but the interference was overcome with an iron dosage of 25 ppm. The effect of Tween 80 could not be overcome with an iron dosage of 50 ppm. Sperry (80) in a study of treatment plant operating records, showed that the great increase in use of household detergents in 1949 and 1950 was coincident with a reduction in the efficiency of primary sedimentation.

Sludge Digestion. There is little information in the literature concerning the effects of synthetic detergents on sludge digestion. It is to be anticipated that if synthetic detergents decrease sedimentation efficiency there would be less sludge removed for digestion and that at any given plant, gas production would diminish. Sperry (80) found that with increased use of household detergents there was a marked reduction in the

percent of volatile matter in primary and secondary sludges, as well as in the volume of gas produced per pound of volatile material added to the digesters and per capita tributary to the plant. At Batavia, Illinois (4), the aeration tank frothing attributed to synthetic detergents coincided with a black, sticky, odorous digested sludge that was very slow drying and very hard when dried. Degens et al (18) studied the effects of a primary and a secondary sodium alkyl sulfate, an alkyl aryl sulfonate and a nonionic typified by a polyglycol ether of an alkylated phenol on sludge digestion. They stated that although the methane yield per gram of carbon is the same for the synthetic surfactants as for soap, less of the surfactant goes into the raw sludge. Hence there is less digestible material causing a reduction in methane production. They also stated that concentrations of pure surfactant less than 500 ppm in the raw sludge did not affect methane production. However, Manganelli (65) reported that 100 ppm of Nacconol PR and Tween 80 slightly inhibited gas production.

Trickling Filters. It has been stated (30) that due to synthetic detergent interference with coagulation, the increased loading to the trickling filters has resulted in ponding. The only occurrence of such clogging that has been found in the literature was the laboratory experiments of Goldthorpe and Nixon at Huddersfield, England (37). In these experiments the sewage used was a mixture of approximately equal parts of domestic sewage and textile industry (wool and yarn scouring) wastes, with a concentration of 5-10 ppm of anionic surfactant. The detergent (Teopol X or Lissapol E) was added in the amount of 200 ppm and allowed to stand for one hour. The sewage was then acidified, flocculated, settled and the supernatant drawn off for feed to the filters. It should be noted that Goldthorpe and Nixon had previously reported that 200 ppm of Teopol almost completely inhibited

acid precipitation. The filters gradually deteriorated, the effluents had gradually increasing B.O.D. concentrations and the filters were badly clogged within 4 to 6 months. Hurley (50), in continuation of his earlier work at Wolverhampton, increased the Teepol loading on his plant to 100 ppm for 4 months with no operational difficulties and with effluents of excellent quality. Lumb (59) experimented with the effect of Santomorse 1 (alkyl aryl sulfonate, 40% active) and Lissapol N (anionic ethylene oxide condensate, 27% active) on laboratory trickling filters. The settled sewage used for feed never contained more than 10 ppm of anionic detergent expressed as Santomorse 1. Detergents were added at rates of 20, 30, 40 and 60 ppm. At 30 ppm the B.O.D. of the effluent was significantly increased, particularly with Santomorse. No significant effects on nitrification, on filter appearance or surface growths were evident. Sperry (80), showed that increased use of synthetic detergents corresponded with a decrease in efficiency of trickling filters in removal of suspended solids and B.O.D.

Activated Sludge. Apparently there is considerable difference in the effect of various synthetic detergents on the activated sludge process. Gaillard (33) stated that Teepol and Lissapol N in amounts of 100 ppm had no visible effect on effluent quality, although there was a slight drop in nitrate content, and no apparent effect on sludge activity. Santomorse caused a progressive deterioration in quality of the effluent and the activated sludge. All protozoan organisms disappeared from the sludge. Lumb (59) in his experiments on the effects of Santomorse 1 and Lissapol N on activated sludge found that with 60 ppm of these detergents the effluents became opalescent, the sludge darker in color and the sludge protozoa few in number. After stopping detergent addition the sludge that had been

treating Lissapol recovered in three weeks, but the sludge that had been treating Santomerse did not recover in six weeks and at the end of that time still showed a lack of active protozoa. Manganielli (65) stated that 100 ppm of Macconol NR, an alkyl aryl sulfonate, caused rapid deterioration of the sludge and its oxidizing ability. Low concentrations, present continuously, induced the same results. Tween 80, a nonionic and biologically oxidizable, had no effect. Tests of the effect on nitrification of repeated additions of synthetic detergents in concentrations of 10 to 100 ppm to activated sludge-sewage mixtures showed that nitrification was suppressed within 48 hours by Macconol, but not by Tween. Addition of Macconol in concentrations of 20 ppm or more completely inhibited nitrification in 5 days.

REMOVAL OF SURFACTANTS BY SEWAGE TREATMENT.

There are marked differences in the effect of biological oxidation processes of sewage treatment on different surfactants. The alkyl sulfates appear to be quite amenable to biological treatment, but the alkyl aryl sulfonates are much more resistant. Hurley (46) in reporting on plant scale experiments stated that during the period when 75 ppm of Teopol (a secondary sodium alkyl sulfate) was added to the sewage flow 91% of the initial Teopol was removed by sedimentation and 64% by the trickling filters and final settling. He also reported (50) that during the period in which 150 ppm were added there was no significant amount of the surfactant in the final effluent and that most of the material was removed in the top foot of the filter. Degens, van der Zee and Komor (20) stated that the alkyl sulfates were almost completely removed by biological treatment, but that a large proportion of the alkyl aryl sulfonates appeared in the final effluent. Zoofer (54), in reporting on the results of five days sampling at Baltimore,

reported that 39% of the initial "sulfonated surface active compounds" were removed by primary sedimentation-trickling filter plant and 21% by primary sedimentation-activated sludge. Lamb (59), experimenting with Santomorse 1 (alkyl aryl sulfonate) on laboratory trickling filters, stated that about 60% of the Santomorse was removed by the filter. There has been little information in the literature on the effect of sewage treatment processes on the nonionic detergents. Mackenzie (64) referred to Imperial Chemical Industries Technical Monograph No. 3 which stated that nonionics such as Lissapol N (ethylene oxide condensate) passed through bio-aeration processes unchanged. Manganelli (65) experimented with the nonionic Tween 80, a polyoxyethylene sorbitan monooleate, and stated that it was biologically oxidizable.

Sawyer et al (76) state that all forms of manufactured surfactants are attacked by bacteria in some degree. The rate and extent of oxidation vary considerably depending upon the structure and size of the surfactant molecule. The alkyl aryl sulfonates and the alkyl phenoxy polyethoxy ethanol types showed some utilization as bacterial food, but are so slowly stabilized that it is impossible to consider removing them in conventional activated sludge practice. The alkyl sulfates, sulfonated fatty acid esters and certain ethylene oxide fatty acid amides and amines are subject to rapid aerobic biological stabilization.

NATURAL WATERS.

Very little information has appeared in the literature on the effect of synthetic detergents on the natural waters. Sawyer (74) stated that phosphorus is a key element in fertilization of natural bodies of water and that the phosphorus content of domestic sewage is about twice what it was before the advent of synthetic detergents.

Coin (14) cites surface tension measurements made over the period from November 1950 to November 1951 on sewage plant effluent and the waters of the Seine, Oise and Marne Rivers. The sewage plant effluent consistently had a surface tension of around 50 dynes per centimeter. The river waters varied from about 70 dynes per centimeter in November 1950 to about 62 in November 1951.

Degens (19) states that anionics of the alkyl sulfate type are quickly decomposed in an aquarium tank, the active material content dropping from 25 to 3 ppm in 4 days, but that biological decomposition of alkyl aryl sulfonates and nonionics proceeds much more slowly, being reduced only 50 percent in 14 days. He found that 5 ppm of the active ingredient of any of these detergents was lethal to tadpoles, sticklebacks and Daphnia in 10-100 hours. With certain types of fish, gradually acclimatized to detergents, the lethal concentration of active material varies from 9 to 36 ppm, although the same types of fish immediately introduced into a 5 ppm concentration died within about 5 hours.

MacKenzie (64) mentions foaming on rivers as a nuisance and stated that in at least one case it has been the subject of an injunction suit in court.

Oldham (68) made tests of the effect of the nonionic surfactant Lissapol N in concentrations of 20 to 50 ppm on carp in aquaria. Two out of four carp showed distress after 2 hrs. in a concentration of 20 ppm, but recovered in fresh water and showed no further distress when returned to the Lissapol solution. After 5 weeks in a concentration of 20 ppm of Lissapol, the concentration was increased to 25 ppm and later to 50 ppm without ill effects on the fish or aquaria plants even after 4 months at the highest concentration.

WATER TREATMENT.

Synthetic detergents have been blamed for difficulties encountered in the operation of water treatment plants at Appleton, Wisconsin (34); Osawatomie, Kansas (16); Wheeling, West Virginia (84) (85) and Omaha, Nebraska (7). Galleher (34) reported difficulties in coagulation and a finished water having taste and odor which were abnormal in that they resisted removal by activated carbon. Culp and Stoltenberg (16) reported extreme difficulties at Osawatomie. At the time of the worst trouble the normal treatment procedures resulted in an estimated 70% of the floc rising to the surface of the coagulation and settling tanks, and 20% carrying onto the filters. As the result filter runs were shortened from 100 to 7 hours. The finished water had a strong, fishy taste. Todd (84) (85) at Wheeling experienced foam to a depth of 4 feet on the raw water basin, difficulty in coagulation and settling, inability to remove iron, and failure to remove taste even when chlorine dioxide dosage was increased to four times normal. The bad taste of the Omaha, Nebraska (7), water was blamed on oil, which resulted from the break of an oil pipeline across the Missouri River, becoming emulsified with the water due to the presence of synthetic detergents in the river water. In the emulsified state the oil was not removed at point of water intake or by flotation on the treatment tanks.

That concentration of synthetic detergents, or their surfactant content, in raw water which results in operational problems has not been established. Galleher estimated it to be only 0.25 ppm at Appleton. The Wheeling and Osawatomie water plants experienced problems when the synthetic detergent concentrations reached approximately 4.0 ppm. However, Culp (17) noted only a minor problem of thin scum on settling tanks

at the Erie, Kansas, plant when the synthetic detergent concentrations were determined to be 5.5 and 8.4 ppm. Cross (15) in reporting on laboratory studies using various coagulants in Lake Michigan water noted that interference with coagulation usually was not observable at levels below 5 ppm. Filichy, Amen and Hassler (23) reported that additions of 0.4 to 3.0 ppm, depending on the particular industrial surfactant used, caused perceptible tastes and odors in spring water, and that in most cases concentrations of 5 ppm would cause taste and odor problems.

Vaughn (86), in testing a sample of ammonium sulfate which contained $1\frac{1}{2}\%$ alkyl aryl sulfonate as an anti-caking agent, found 16 ppm ammonium sulfate (0.2 ppm alkyl aryl sulfonate) caused interference with coagulation and resulted in the development of a disagreeable chemical-type odor not removable by the normal chlorination (4 parts chlorine to 1 part ammonia) process.

Cross (15) studied the use of alum, alum-silicate, ferric sulfate and chlorinated coprecipitates, each with and without lime, for coagulation of water containing various synthetic detergents. He found that without lime the alum-silicate was the best coagulant, and that the addition of lime improved coagulation in all cases. Culp and Stoltenberg (16) found 25 ppm alum and 1 ppm activated silica gave the best results in their laboratory studies, and used that dosage for emergency operation of the Osawatomie plant. Todd (85) noted that a pH of 10.3, which would require four times the normal lime dosage, would have been necessary to remove iron from the Wheeling water.

In so far as known, none of the above-mentioned investigators considered the possible effect of appreciable concentrations of the complex, anhydrous phosphates, which are commonly present in anionic

household synthetic detergents in amounts up to 40 or more per cent by weight. Such phosphates may increase the surface activity of wetting agents; form complexes with ions of earth alkalies and heavy metal salts; and also peptize, disperse, suspend and emulsify pigments, oils, etc. In water treatment (90) hexametaphosphate dosages as low as 0.5 ppm have been used successfully in preventing deposition of lime; also certain commercial phosphates are frequently used in dosages around 2 ppm to prevent iron and manganese stains on plumbing fixtures, laundry, etc. Langolier et al (56) studied the effect of sodium metaphosphate on the alum dosage required for good flocculation of water containing 0.5 milliequivalents per liter of alkalinity and 60 ppm turbidity. Within the range from 0 to 5 ppm they found it desirable to increase the alum dosage approximately 5 ppm for each 1 ppm sodium metaphosphate present in the water. When metaphosphate concentrations exceeded 5 ppm, they were unable to secure effective alum coagulation regardless of the amount of alum added.

Except for the Osawatomic experience, during which filter runs were reduced from 100 to 7 hours duration, no information has been found in the literature on the effect of synthetic detergents on filtration. However, any factor adversely affecting coagulation and sedimentation will tend to increase the load on the filter and thus shorten the runs.

Experience with taste and odor problems resulting from treatment of water containing synthetic detergents has varied greatly. Gallaher (34) reported the failure to remove abnormal moldy or mildewy taste in Appleton water with activated carbon. Although the dosages tried were not given, they must have been substantial since he mentions maximum dosages during the summer of 40 to 80 ppm. However, chlorine dioxide

(0.35 to 0.6 ppm sodium chlorite plus chlorine) eliminated all consumer complaints. Todd (85) reported the elimination of odor, but not of taste, with dosages of either 40 ppm activated carbon, or with chlorine dioxide (1.5 ppm sodium chlorite plus chlorine). In laboratory studies made in connection with the Osawatomic experience, Culp and Stoltenberg found either 40 ppm activated carbon or "breakpoint" chlorination (10 ppm) eliminated taste and odor of the water. However, when the plant was operated with 10 ppm applied chlorine the finished water had a less intense, but bitter, soapy taste. Drawing on Gallaher's experience they applied 10 ppm chlorine to the rapid mix tank followed by 2 ppm (later reduced to 1 ppm) chlorine dioxide to the filter influent. Immediate improvement in taste and odor of the water was noted, and in a few days all consumer complaints ceased. Filicky et al. (28) (29) studied the effectiveness of chlorination, chlorine dioxide, and activated carbon in removing taste and odor from taste and odor free spring water to which 5 ppm bland lard and 5 ppm of detergent had been added. Five different industrial surfactants, representing four types of anionics were used. Chlorine (10 ppm) followed by dechlorination was ineffective. Treatment with chlorine dioxide (2 ppm) followed by 16 hours contact time and dechlorination gave no better results. However, treatment with 80 ppm activated carbon eliminated all tastes from 4 of the detergents and about 80% of the taste developed with the fifth detergent. It substantially reduced, but did not eliminate the odor of the waters. They reported that the activated carbon was most effective when the pH of the water ranged from 5 to 8, also that the activated carbon should be applied ahead of chlorination. Culp (17), however, noted that the finished water at Erie, Kansas, although it foamed moderately and contained 6.0 and 9.8 ppm of household synthetic detergents,

had no objectionable taste.

Hopper and McCowen (47) have suggested the flotation process for water treatment. In laboratory studies they added 10 ppm of cationic surfactant (quaternary ammonium compound) and aerated at the rate of $1\frac{1}{2}$ liters per liter per minute for from 3 to 5 minutes. They reported a remarkable reduction in turbidity, bacteria and cysts of *E. Histolytica*. The finished but unchlorinated water was clear and sparkling and had no taste and odor. It contained only about 1 ppm of the quaternary ammonium compound.

Water treatment processes as used for producing public water supplies do not remove any appreciable amounts of the surfactants used in synthetic detergents. Culp and Stoltenberg (16) noted that the household synthetic detergent concentrations in raw and finished water at Osawatomie as being 3.9 and 3.6 ppm, respectively. Culp (17) reported data for two days at Erie as follows:

Date	Household Synthetic Detergent Concentration	
	Raw Water	Tap Water
January 7, 1954	8.4 ppm	9.8 ppm
January 14, 1954	5.5 ppm	6.0 ppm

Todd (85) found that the treatment at Wheeling effected about 20% reduction in the synthetic detergents. Thus, it is reasonable to believe that surfactants, equivalent in amounts to several parts per million of household synthetic detergents, may occur in domestic and industrial water supplies.

Certain problems may result from the presence of surfactants in domestic and industrial water supplies. Todd (84) and Mackenzie (64) have raised the question of the health of humans consuming synthetic detergent contaminated water over an extended period of time. Todd also noted complaints of difficulty in regenerating water softeners

and death of tropical fish during the Wheeling experience. Vaughn (87) has noted three instances of trouble with foaming in plant boilers which were blamed on water contaminated with synthetic detergents.

TOXICITY.

A limited review of the literature has revealed one and possibly two cases of fatal poisoning of a human resulting from ingestion of a synthetic detergent. Adelson and Sunshine (1) reported the death of a 45 year old woman who drank less than one ounce (28.3 gm) of an aqueous solution containing 10% of the cationic surfactant, methyl dodecyl benzyltrimethyl ammonium chloride. Mackenzie (64) noted a similar or the same case.

Fogelson and Shock (32) treated patients having gastroduodenal ulcerative disease with sodium alkyl sulfato. The treatment consisted of administering 0.2 gm of sodium alkyl sulfato every two hours throughout the day. At least one patient was treated for over a month. These authors reported no toxic effects occurred in either man or experimental animal in seven months' administration of this dose. Furthermore, Fogelson took 1 gm of the above mentioned surfactant daily for eight weeks without any toxic effect.

Janowitz et al studied the effect of two nonionic surfactants on the gastro-intestinal motility of man. Twenty-four normal individuals of both sexes, and ages ranging from 16 to 53 years, were divided into two groups. One group was fed "Tween-65", and the other group "Tween-80". Each individual ingested 3 gm of surfactant with each meal (9 gm daily) for two weeks without showing any evidence of gastro-intestinal disturbance, change in nutritional status, or significant variation in weight.

Numerous investigators (10), (31), (35), (79), (88) have studied the relative toxicity of various manufactured surfactants as determined

using mice, rats, rabbits, dogs, and in one case monkeys as test animals.

Hopper, Hulpieu and Cole (46) reported on both acute and subacute toxicity of 8 anionic, 3 nonionic, and 4 cationic surfactants. Acute toxicity, as determined using mice dosed by stomach tube, expressed in terms of LD_{50} , ranged as follows:

anionics	2.00 to $\neq$ 25.0 gm/kg of weight
nonionics	3.50 to $\neq$ 24.0 gm/kg of weight
cationics	0.34 to 2.00 gm/kg of weight

Subacute toxicity to mice was determined by the same method, except that 0.1 LD_{50} doses were given daily for six days of each week. For three surfactants the LD_{50} subacute toxicity level was less than the LD_{50} acute toxic level. For eight of the surfactants it exceeded 2.5 times the acute LD_{50} level. Subacute ranges in terms of LD_{50} were as follows:

anionics	$\neq$ 2.00 to $\neq$ 25.0 gm/kg of weight
nonionics	$\neq$ 3.50 to $\neq$ 25.0 gm/kg of weight
cationics	0.30 to ? gm/kg of weight

Woodard and Celvery (92) summarized data from their experiments and from the literature. Acute toxicity for oral ingestion expressed in terms of LD_{50} ranged as follows:

For mice: 1.5 to 12.6 gm/kg weight for 7 anionics.

For rats: 1.0 to 4.0 gm/kg weight for 8 anionics.

For Guinea Pigs: 0.4 to 1.5 gm/kg weight for 3 anionics.

and the LD_{50} dose for rats for the only cationic tested, alkyl dimethyl benzyl ammonium chloride was 0.35 gm/kg of weight. These same authors reported limited data on repeated doses. A cationic, alkyl dimethyl benzyl ammonium chloride, was again found to be the most toxic.

About the only conclusions that may be drawn from these data are:

- (1) The cationics are the most toxic of the surfactants.
- (2) In general, the toxicities of the nonionics and anionics are of the same order.
- (3) The toxicities of the various surfactants within any given class, and even of the same type, may vary greatly.

After summarizing the available information on toxicity of surface active agents, Woodard and Calvery (92) stated, "We are appalled by the many unanswered questions concerning the toxicological properties of surface-active agents. A major contributing factor to this paucity of information is undoubtedly the fact that the majority of the commercially surface-active agents are not reproducible chemical entities. They are in some cases impure, sometimes variable from batch to batch, and often mixtures of closely related analogues." Moreover, many investigators in reporting on their work have identified the surfactant studied under a general group name, such as alkyl aryl sulfonate or alkyl sulfate, without consideration as to whether the results obtained are representative for that general group.

Although available information indicates that the problem of ingestion of synthetic detergents in drinking water is not too serious, additional study of the problem is considered advisable. The available data are inadequate when one considers the seriousness of the problem, also the large number and variability of the toxic levels of the surfactants used in synthetic detergents.

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